

1.131.631



PATENT SPECIFICATION

NO DRAWINGS

1.131.631

Inventors: PHINEAS DAVIES, ALAN JAMES HALL and
DENNIS ALBERT DOWDEN

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Act 1949): 3 Dec., 1965.

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COMPLETE SPECIFICATION

Catalysts of High Activity at Low Temperature

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company of Imperial Chemical House, Millbank, London S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the reaction of carbon monoxide with steam over catalysts of high activity at low temperature. The catalysts in preferred forms have the advantage of remaining active for longer periods of use, or of being less dense without serious loss of mechanical strength, than many previously known related catalysts.

According to the invention there is provided a process for reacting carbon monoxide with steam at temperatures below 300° C. over a catalyst comprising the product of reducing partly the co-precipitated oxides of copper and zinc and at least one further metal selected from manganese and the metals of Groups II to V of the Periodic Table whose oxides are difficultly reducible.

By metals of Groups II to V of the Periodic Table whose oxides are difficultly reducible we mean, in this specification, metals of Groups II to V whose oxides are more difficult to reduce than manganese dioxide.

Metals whose oxides are difficultly reducible occur above Manganese in the electromotive force series of elements (see "Handbook of Chemistry and Physics" (Chemical Rubber Publishing Co., Cleveland, Ohio), 32nd Edition, pages 1521—3.)

Certain catalysts to be used in the process of the invention and the compositions from which they can be made by reduction are believed to be new compositions of matter. Therefore as further features the invention provides such catalysts, the compositions from

which can be made by reduction and a method for making the catalysts and compositions as set forth hereinafter. In the catalyst to be used in the process of the invention the further metal if not manganese is preferably a metal from Group II or Group III of the Periodic Table, particularly aluminium or magnesium, although titanium or zirconium or thorium can be used. The proportion of the oxide of manganese or the further metal is preferably in the range 4 to 20 especially 8 to 20% by atoms of the total of the oxides mentioned. If manganese oxide is present its valency is preferably not greater than 4 in the catalyst as normally handled, that is, before reduction preliminary to use or in use.

The copper content of the catalyst or composition is preferably at least 10% for example in the range 10 to 70% especially 10—50%. The zinc content is preferably at least 20%, for example between 20% and 80%. Thus suitable catalysts contain copper, zinc and the further metal or metals in the ratios 30:60:10, 40:40:20 and 60:30:10 and ratios intermediate of these ratios. These proportions are also by atoms.

The process of the invention is especially advantageous when the catalyst has been made by reducing a composition made by co-precipitation from non-halide sulphur-free soluble salts of the metals by means of a carbonate or bicarbonate of an alkali metal or (less preferably) an ammonium, whereafter the resulting precipitate is washed substantially free of alkali, dried and calcined. The mixing of the solutions in the precipitation stage is preferably performed continuously. The temperature of the mixing stage is preferably in the range 65 to 85° C., and preferably it is raised to 80 to 100° C. after mixing and kept there until the pH ceases to rise. Preferably a fairly low but constant degree of alkalinity (corres-

SEE ERRATA SLIP ATTACHED

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ERRATUM

SPECIFICATION No. 1,131,631

Page 1, line 43, after "which" insert "they"
THE PATENT OFFICE
10th April 1969

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ponding to a pH at 90° C. in the range up to 9.0 especially up to 8.0) is maintained during and after the precipitation. (In the provisional specification the lower limit 7.0 was quoted in the sense of "neutrality" although, at the temperatures used, neutrality may be at a pH as low as about 6.0). The washing of the precipitate, if made using an alkali metal compound, should preferably be so as to leave less than 0.5% of alkali metal oxide (calculated as Na₂O), more preferably less than 0.2%.

In the above method it is preferred that at least some and preferably all the content of each metallic constituent introduced by precipitation should be introduced as a compound in which it is present as cations especially as nitrate or acetate. It is however within the scope of the invention to introduce one or more metallic constituents as anions. The calcination of the precipitate is preferably at temperatures up to 350° C. for example about 300° C.

If the catalyst is to be used in a static bed it can be formed into shapes for example by granulation, pelleting or extrusion. These operations are carried out preferably after calcining the precipitate. The pellet density of the composition is preferably in the range 1.0 to 2.0 especially 1.4 to 1.8. Before being brought into use the catalyst composition is reduced to give the active form; and this is usually done by the user of the catalyst in the converter in which it is to be used. Reducing gases such as hydrogen or carbon monoxide, preferably substantially diluted with a gas inert to the catalyst such as nitrogen or steam, can be used for the reduction provided they are substantially free of sulphur and other catalyst poisons. A suitable reduction temperature is 230°; excessive temperatures should of course be avoided.

The catalyst composition to be used in the process of the invention preferably contains, in addition to the oxides introduced by co-precipitation, a proportion of catalyst support material which is not introduced by co-precipitation. Suitably this material is chemically the same as the oxides introduced by co-precipitation, although it need not be. Preferably the major proportion of catalyst support material is introduced by co-precipitation. An especially good catalyst contains 2 to 8% w/w of added alumina, and this has preferably been added in the form of an alumina hydrate or a hydratable alumina to one or more of the solutions taking part in the co-precipitation, so that precipitation takes place in its presence. The catalyst composition according to the invention may if desired contain a proportion of chromium oxide, preferably up to about 25% of the total composition, and this is preferably introduced by co-precipitation. Both the above-mentioned percentages are by

weight on the oxides present in the catalyst composition when in the oxide form.

The new catalysts and compositions are those derived from the carbonates of copper and zinc and containing 10–50% by atoms of copper, and corresponding catalysts and compositions embodying the various preferred features herein defined.

In the process for reacting carbon monoxide with steam the catalyst is deactivated by excessive temperatures, hence the process is operated at temperatures up to 300° C. Pressures over a wide range, for example 1 to 50 atmospheres and higher, can be used. The inlet gas should be substantially sulphur free, that is, contain less than 5, especially less than 1 part per million by weight of sulphur free or combined, hence it is expedient to protect the catalyst by means of a sulphur-absorbing bed or other "guard case", conveniently one operative at the inlet temperature of the catalyst. The process of the invention is very conveniently used to treat a gas mixture whose CO content has been decreased (e.g. to less than 5%) over a catalyst (such as iron oxide or a molybdate) which is effective at higher temperatures. Such two-stage carbon monoxide conversion systems are already well known. The process of the invention can be used in conjunction with known process steps for adjusting the steam concentration and temperature and for removing carbon dioxide.

In the production of ammonia synthesis gas or hydrogen the process of the invention is particularly applicable for converting to carbon dioxide the carbon monoxide in a crude gas obtained by reaction of a carbonaceous or in the feedstock with steam, whereafter the carbon dioxide is removed by known means. The process can also be used for the removal of carbon monoxide from a fuel gas generated by reacting a carbonaceous feedstock with atoms in order to decrease the toxicity of such a gas.

The invention is illustrated by the following Examples.

EXAMPLE 1

A solution (4 litres) of cupric nitrate trihydrate (0.694 kg.), zinc nitrate hexahydrate (1.323 kg.) and aluminium nitrate nonahydrate (0.853 kg.) in water was mixed continuously at 74° C. with a solution (20 litres) of sodium carbonate (3.4 kg. as Na₂CO₃). The rates of flow during the mixing were such as to afford a small excess of alkali, corresponding to a slurry pH of 7.0 to 7.5. The whole slurry was then diluted with 10 litres of water, heated to 90° C. and held there for 1 hour. It was observed that as a result of this heat-treatment the pH of the slurry rose to 8.4. The precipitate was collected on a filter, re-slurried with 20 litres of water, then collected again and washed with 30 litres of water. The filter cake was dried

- at 120° C. calcined at 300° C. for 8 hours, then finely powdered. A sample of it was pelleted with 2% of graphite to give 3/16 x 3/16 inch cylindrical pellets. The percentage composition of the pellets by weight was as follows:
- CuO 28.6
ZnO 44.5
Al₂O₃ 12.5
- 10 Loss at 900° 15.1 (includes volatiles and graphite).
This corresponds to an atomic ratio of 35% copper, 53% zinc and 12% aluminium. The pellets had a mean vertical crushing strength of 369 pounds, pellet density of 1.91 and a bulk density of 1.2.
- A sample of the composition was tested as pellets by reducing it with dilute hydrogen (1.5% H₂, 98.5% N₂) at 230° C., then passing over it a mixture of steam (33.3%), carbon monoxide (3.3%), carbon dioxide (10%) and hydrogen (33.3%) at atmospheric pressure and at a space velocity of 22,500 litres per kg. of catalyst per hour. A catalyst containing only copper and zinc (34:66 by moles respectively) and having a mean vertical crushing strength of 150 pounds, a pellet density of 2.46 and a bulk density of 1.5 was tested in the same way. The activity of the catalysts at 240° C., expressed as rate constants based on the rate of destruction of carbon monoxide, is given in the Table: the values in brackets are percentages of initial activity.

TABLE 1

Time (hours)	Activity (sec ⁻¹)	
	Cu — Zn — Al	Cu — Zn
0	7.8 (100)	12.5 (100)
100	7.3 (93.5)	10.2 (81.5)
300	7.0 (89.8)	8.4 (67.2)
500	6.6 (84.6)	7.5 (60.0)
1000	5.9 (75.6)	6.5 (52.5)

- 35 A second sample of the filter cake was pelleted with 2% of graphite but using a lower pelleting pressure. The mean vertical crushing strength of these pellets was 150 pounds and their density was 1.66. When tested in the same way as the higher density catalyst the following activities were recorded.

TABLE 2

Time (hours)	Activity (sec ⁻¹)
0	not available
23	7.8
100	7.6
300	6.8
500	6.8

- The gas mixture used in this Example has a composition representative of a crude hydrogen stream or an ammonium synthesis gas or a fuel gas after a high-temperature carbon monoxide conversion stage.

EXAMPLE 2

The procedure of Example 1 was followed with the exception that 0.256 kg. of magnesium nitrate hexahydrate was used in place of the aluminium nitrate and minor changes were made in the washing of the precipitate. Under the conditions used, magnesium is not completely precipitated, and as a result the magnesium content of the catalyst was less than the aluminium content of the catalyst of Example 1. The percentage composition of the catalyst was

CuO 30.5
ZnO 52.3
MgO 3.0

Loss at 900° C. 14.4 (includes volatiles and graphite).

This corresponds to an atomic ratio of 34.9% copper, 58.4% zinc and 6.7% magnesium. The pellets had a mean vertical crushing strength of 162 pounds, a peller density of 1.66 and a bulk density of 1.11.

In order to test this catalyst the pellets were crushed to pass a 17 B.S.S. sieve but to be retained on a 25 B.S.S. sieve and then reduced by means of a mixture of hydrogen (1.5% by volume) and nitrogen at 230° C. There was then passed over the reduced catalyst a mixture of steam (50%), carbon monoxide (25%) and hydrogen (25%), with a dry gas space velocity of 18000 litres per litre of catalyst-filled space per hour.

The activity of the catalyst in reciprocal second units at 240° C. was as given in Table 3.

TABLE 3

Time (hours)	Activity (sec ⁻¹)
0	10.0
100	8.5
300	6.8

EXAMPLE 3

A solution (4 litres) of cupric nitrate trihydrate (0.694 kg.), zinc nitrate hexahydrate (1.488 kg.) and manganese nitrate hexahydrate (0.143 kg.) in water was mixed continuously at 70° C. with a solution (20 litres) of sodium carbonate (3.4 kg. as Na₂CO₃). The rates of flow during the mixing were such as to afford a small excess of alkali, corresponding to a slurry pH of 7.0 to 7.5. The whole slurry was then diluted with 6 litres of water, heated to 90° C. and held there for ½ hour. It was observed that as a result of this heat-treatment the pH of the slurry rose to 8.7. The precipitate was collected on a filter, re-slurried with 20 litres of water, then collected again and washed with 20 litres of water. The filter cake was dried at 120° C. calcined at 300° C. for 8 hours, then finely powdered. A sample of it was pelleted with 2% of graphite to give 3/16 x 3/16 inch cylindrical pellets. The percentage composition of the pellets by weight was: CuO 29.0, ZnO 54.7, MnO 5.3, loss at 900° C. 10.5 (includes volatiles and graphite). This corresponds to an atomic ratio of 32.2 copper, 59.4 zinc and 8.4 manganese. The pellets had a mean vertical crushing strength of 115 pounds, a pellet density of 1.55 and a bulk density of 1.0.

A sample of the pelleted composition was reduced and tested as described in Example

1 using as standard a further sample of the same copper-zinc catalyst.

The conversion at 230° C. was 32.5%, for the copper-zinc-manganese catalyst, and 30% for the copper-zinc catalyst; these results were using the same weight of each catalyst, although the copper-zinc catalyst is considerably the denser. The activity of the catalysts, expressed as rate constants based on the rate of destruction of carbon monoxide at 240° C., was 9.6 sec⁻¹ for the copper-zinc-manganese catalyst and 12.5 sec⁻¹ for the copper-zinc catalyst. However although the activity of the copper-zinc-manganese catalyst was less than that of the copper-zinc catalyst, this was the initial activity, and after a few weeks' use the copper-zinc-manganese catalyst was the more active.

EXAMPLE 4

The procedure of Example 3 was followed with the exception that 0.286 kg. of manganese nitrate hexahydrate was used instead of 0.143 kg. and 1,323 kg. of zinc nitrate hexahydrate in place of 1.488 kg. The pellets had a mean vertical crushing strength of 134 pounds, a pellet density of 1.68 and a bulk density of 1.07.

The percentage composition of these pellets by weight, was CuO 28.7, ZnO 47.6, MnO 10.6, loss at 900° C. 12.0. This corresponds

to an atomic ratio of 32.8 copper, 53.5 zinc and 13.6 manganese.

The catalyst was tested as described in

Example 1, using as standard a further sample of the same copper-zinc catalyst and the results are shown in Table 4.

TABLE 4

Time (hours)	Activity (sec ⁻¹)	
	Cu — Zn — Mn	Cu — Zn
1	11.5	12.5
200	11.0	8.8
350	10.2	8.0
600	9.4	7.2
1000	8.9	6.7
1600	8.2	5.8

Evidently the manganese-containing catalyst, although slightly inferior in initial activity, is much the more active after prolonged use.

EXAMPLE 5

To a solution of copper nitrate trihydrate (1.04 kg.), zinc nitrate hexahydrate (2.56 kg.) and concentrated nitric acid (400 ml.) in 3 litres of water there were added 0.19 kg. of sodium aluminate in 600 ml. water. Alumina was precipitated but redissolved on stirring. Then 0.075 kg. of finely divided solid alumina trihydrate was added. The resulting suspension was mixed at a flowing junction with a sodium carbonate solution sufficient to give a pH of 7.0 to 8.0 at the precipitation temperature which was 70° C. The slurry was diluted with 6 litres of water, heated at 90° C. for 1 hour (final pH 8.5), then filtered. The washing, calcining and pelleting procedure were as described in Example 1. The pellets (5.4 mm. diameter, 3.6 mm. long) had a mean vertical crushing strength of 187 lbs., a pellet density of 1.56 and a bulk density of 0.99. The percentage composition of the pellets was

CuO 22.2
 ZnO 47.0
 Al₂O₃ 10.7 (7.2 by precipitation, 3.6 added solid)
 Na₂O 0.11
 Loss at 900° C. 19.4

This corresponds to an atomic ratio of 29% copper, 60% zinc, 11% aluminium.

The pellets were crushed and tested as described in Example 2. At 200° C. the conversion was 32% and at 250° C. 51%.

WHAT WE CLAIM IS:—

1. A process for reacting carbon monoxide

with steam at temperatures below 300° C. over a catalyst comprising the product of reducing partly the co-precipitated oxides of copper and zinc and at least one further metal selected from manganese and the metals of Groups II to V of the Periodic Table whose oxides are difficultly reducible.

2. A process according to claim 1 in which the further metal of the catalyst is from Group II or Group III of the Periodic Table or is manganese.

3. A process according to claim 2 in which the further metal of the catalyst is aluminium, magnesium or manganese.

4. A process according to any one of the preceding claims in which in the catalyst the proportion of the further metal or metals is in the range 4 to 20 especially 8 to 20% by atoms.

5. A process according to any one of the preceding claims in which in the catalyst the proportion of copper is in the range 10 to 70% by atoms.

6. A process according to claim 5 in which in the catalyst the proportion of copper is in the range 10 to 50% by atoms.

7. A process according to any one of the preceding claims in which in the catalyst the proportion of zinc is at least 20% by atoms.

8. A process according to any one of the preceding claims in which the catalyst contains, in addition to the oxides introduced by co-precipitation, a proportion of catalyst support material not so introduced.

9. A process according to claim 8 in which the catalyst, the major proportion of the catalyst apart from its copper and zinc content has been introduced by co-precipitation.

10. A process according to claim 9 in which

the catalyst support material not introduced by co-precipitation is chemically the same as the oxides so introduced.

5 11. A process according to claim 10 in which the catalyst support material not introduced by co-precipitation is alumina introduced as an alumina hydrate or a hydratable alumina and constitutes 2 to 8% by weight of the catalyst.

10 12. A process according to any one of claims 1 to 11 in which the catalyst has been made by co-precipitating the oxides of copper and zinc and at least one further metal selected from manganese and the metals of Groups II
15 to V of the Periodic Table whose oxides are difficultly reducible from the non-halide sulphur-free soluble salts of these metals by means of a carbonate or bicarbonate of an alkali metal or an ammonium, whereafter the resulting precipitate is washed substantially free of soluble
20 salts, dried and calcined.

13. A process according to claim 12 in which the catalyst is one in the making of which an alkali metal carbonate or bicarbonate has been used and the making of the precipitate has been so as to leave less than 0.2%
25 of alkali metal oxide calculated as Na_2O in the precipitate.

14. A process according to claim 12 or
30 claim 13 in which the catalyst is one in the making of which the mixing of the reacting solutions was performed continuously.

15. A process according to any one of claims 12 to 14 in which the said mixing was
35 at a temperature in the range 65 to 85° C.

16. A process according to any one of claims 12 to 15 in which the catalyst is one in the making of which the pH during and after the precipitation was maintained at between
40 neutrality and 2.0 units on the alkaline side of neutrality.

17. A process according to any one of claims 12 to 16 in which the catalyst is one in the making of which the temperature of the reacting
45 solutions was after mixing raised to 80

to 100° C. and kept there until the pH ceased to rise.

18. A process according to any one of claims 12 to 17 in which the catalyst is one in the making of which all the content of each metallic constituent introduced by precipitation was introduced as a compound in which it is present as cations. 50

19. A process according to any one of claims 12 to 18 in which the catalyst is one in the making of which the co-precipitation was performed in the presence of catalyst support material amounting to 2 to 8% by weight of the oxides of the total catalyst composition. 55

20. A process according to any one of claims 12 to 19 in which the pellet density of the catalyst composition before reduction was in the range 1.0 to 2.0 especially 1.4 to 1.8. 60

21. A process according to claim 1 substantially as described and as set forth in any one of the foregoing Examples. 65

22. A process for producing ammonia synthesis gas or hydrogen or for detoxifying fuel gas which includes reacting carbon monoxide with steam by a process according to any one of claims 1 to 21. 70

23. Hydrogen, ammonia synthesis gas or detoxified fuel gas whenever produced by a process according to claim 22.

24. A catalyst as defined in claim 6, whenever derived from the carbonates of copper and zinc, and optionally including any one of the preferred features of claims 7 to 10. 75

25. A catalyst made by a method defined in any one of claims 12 to 20 and having a copper content in the range 10 to 50% by atoms. 80

26. A catalyst according to claim 24 or 25, substantially as described and as set forth in any one of the foregoing Examples. 85

27. A catalyst composition in oxide form from which a catalyst according to any one of claims 24 to 26 can be made by reduction.

WALTER SCOTT,

Agent for the Applicants.